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Contract: Theory in support of laboratory spectroscopy for AIRS, TES and HIRDLS
Summary of first year's work

Line-Shape Parameters for Water Vapor in the 3.2-17.76 μm Region.

The focus of this theoretical study is to update the molecular line shape parameters in the HITRAN compilation for water and methane in the spectral regions important for AIRS, TES and HIRDLS. In the first year, calculations were made to determine the collision-broadened half-width and collision-induced line shift of water vapor lines in the 3.2-17.76 μm region. The file 01_HIT01.par which contains the water vapor transitions on the HITRAN database was downloaded. Code was written to extract from the file the bands in this region. The bands are listed in Table 1 along with the number of lines in the bands on HITRAN and the number of lines in the wavelength region. The data for the individual bands was written to files where lines with rotational quantum number (upper or lower) greater than 20 were eliminated (5 lines total, 3 from the rotation band and 2 from the ν_2 band). This is necessary because the complex Robert-Bonamy (CRB) formalism calculations are dependent on the vibrational states of the transition. In total there are 13 622 transitions. Additional code was written to read these

files and create input files of the rotational quantum numbers for each band studied in the index code needed by the CRB codes.

Calculations were made for the H_2O-N_2 system for each vibrational band at 225 and 296 K. We are currently completing the calculations for the H_2O-O_2 system. The potential employed in the calculations consists of the leading electrostatic components for the collision system (the dipole and quadrupole moments of H_2O with the quadrupole moment of N_2 or O_2), an atom-atom component [1, 2, 3] and isotropic induction and dispersion components. The isotropic component of the atom-atom potential is used to define the trajectory of the collision within the semi classical model of Robert and Bonamy [4].

The atom-atom potential is defined as the sum of pair-wise Lennard-Jones 6-12 interactions [5] between atoms of the radiating molecule and the perturbing molecule, N_2 or O_2 and is given in terms of the Lennard-Jones parameters for the atomic pairs, ε_{ij} and σ_{ij}. The heteronuclear atom-atom parameters are usually constructed from homonuclear atom-atom parameters (ε_i and σ_i) by "combination rules" [6-9].

For nitrogen broadening of $H_2{}^{16}O$ six transitions were chosen for which there are multiple measurements [10-18] and for which the calculations were too high for two lines, too low for two lines, and in agreement for the last two transitions. The potential parameters were adjusted to give a good fit of all the lines. The parameters are ε_{HN}, σ_{HN}, ε_{ON}, and σ_{ON}. For the starting values the heteronuclear atom-atom parameters used are derived from homonuclear-atom-atom parameters obtained by Bouanich [19] using the combination rules [6]. The final values correspond to a 10% lowering of ε_{ON}, a 10% increase in ε_{HN}, a 3.9% decrease in σ_{HN}, and no change in σ_{ON}. Note, a full least-squares

minimization was not thought worthwhile until the work of Ref. 20 is completed. For oxygen broadening of $H_2{}^{16}O$ there are not multiple measurements to allow fitting to an average. A similar procedure to that used for H_2O-N_2 with some of the data from Ref. 21 was done. The best fit was obtained by lowering σ_{HO} by 10% of the combination rule value. The other atom-atom parameters (ε_{HO}, ε_{OO}, σ_{OO}) are the combination rule values.

The atom-atom potential must be expanded in terms of the center-of-mass internuclear separation, R. The order of the expansion has been discussed by Labani et al. [3] and by Gamache et al. [1, 2, 22]. Here the formulation of Neshyba and Gamache [2] expanded to eighth order is used.

The calculations were made for each ro-vibrational transition at each temperature of the study with either N_2 or O_2 as the perturber gas.

Once the oxygen-broadening calculations are completed, the half-width and line shift for air as the perturbing gas can be obtained assuming binary collisions and Dalton's law

$$\gamma_{air} = 0.79\,\gamma_{N_2} + 0.21\,\gamma_{O_2} \quad \text{and} \quad \delta_{air} = 0.79\,\delta_{N_2} + 0.21\,\delta_{O_2} \,. \tag{1}$$

This must be done for both temperatures of the study.

From the calculations made at the two temperatures, the temperature dependence of the air-broadened half-widths can be determined. The temperature dependence of the half-width was taken as its usual power law form

$$\gamma(T) = \gamma(T_0)\left\{\frac{T_0}{T}\right\}^n , \tag{2}$$

where the reference temperature T_0 is usually taken as 296K but is not restricted to that value.

Code was written to take the data files for each band for nitrogen and oxygen as the perturbing gas and at each temperature apply Eq. (1) to determine the air-broadened half-width and line shift at 225 K and 296 K and then to use these values to determine the temperature dependence of the half-width. The code writes a data file for each band studied. When completed these files will be collected into a single data file and given to Dr. Larry Rothman to be merged later with the measured half-widths for addition to the HITRAN database.

Our effort for the next year is to start calculations for methane perturbed by nitrogen and calculations for self-broadening of water vapor. We will also investigate calculations for water vapor perturbed by nitrogen and oxygen using the velocity averaged form of the CRB formalism. Comparisons with the experimentally determined half-widths and line shifts will also be made.

Table 1. Vibrational bands in the 3.2-17.76 μm region and number of lines in each band.

Band	# lines	# lines in spectral range
(000)←(000)	4528	886
(010)←(010)	1136	152
(010)←(000)	6102	6102
(020)←(010)	1800	1800

(100)←(020)	628	628
(030)←(020)	382	382
(001)←(010)	543	543
(020)←(000)	2720	1490
(030)←(010)	313	146
(100)←(000)	3575	1423
(001)←(010)	4437	75

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